Appendix C

Protocol for SCOS97-NARSTO
Performance Audit and Laboratory Comparison
for Speciated Hydrocarbon Measurements

(Revised May 28, 1997)

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1.0 Purpose and Overview

1.1 Performance audits of hydrocarbon measurements are being conducted as part of an external quality assessment program for the SCOS97-NARSTO Study. The purpose of the audits is to document differences that may exist between laboratories in the SCOS study area (greater than 30% for concentrations of individual species above 1.0 ppbC).

1.2 The audits will consist of a review by Desert Research Institute (DRI) of standard operating procedures (SOPs) used by each measurement group, and performance audits consisting of two to five ambient samples.

2.0 Participants

2.1 Coordination, Data Compilation and Analysis

Desert Research Institute (Dr. Eric Fujita, ericf@sage.dri.edu, 702/677-3311 Fax - 702/677-3157) P.O. Box 60220 (Street Address: 5625 Fox Ave.) Reno, NV 89506

California Air Resources Board (Mike Miguel, mmiguel@arb.ca.gov, 916/322-7054 Fax - 916/322-8217) P.O. Box 2815 Sacramento, CA 95812

2.2 Collection of Ambient Audit Samples

Air Resources Board, Monitoring and Laboratory Division (Pat Harrington, 818/575-6993 Fax – 818/350-6468) 9480 Telstar Ave Suite 4 El Monte, CA 91731.

2.3 Participating Laboratories

(1.) California Air Resources Board, Monitoring and Laboratory Division (Hieu Le, 916/323-4398; Fax – 916/327-8217) 1309 T Street Sacramento, CA 95812

(2.) U.S. EPA National Exposure Research Laboratory (Bill Lonneman, 919/541-3895; Fax - 919/541-4787) mailing address: MailDrop 84 Research Triangle Park, NC 27711 shipping address for canisters: EPA Tech Center Alexander Drive & Highway 54 Research Triangle Park, NC 27711

(3.) Biospheric Research Corporation (Dr. Rei Rasmussen, rrasmus@ese.ogi.edu, 503/690-1077; Fax - 503/690-1669) 17010 N.W. Skyline Blvd. Portland, Oregon 97231

(4.) Desert Research Institute (Dr. Barbara Zielinska, e-mail: barbz@sage.dri.edu, 702/6773198; Fax – 702/677-3157) mailing address: P.O. Box 60220 Reno, NV 89506 shipping address: 5625 Fox Avenue Reno, NV 89506

(5.) San Diego Air Pollution Control District (Mahmood Hossain, mhossain@ sdapcd.co.san-diego.ca.us, 619/694-3358 Fax 619/694-2730) 9150 Chesapeake Dr. San Diego, CA 92123-1026.

(6.) South Coast Air Quality Management District (Steve Barbosa, sbarbosa@ aqmd.gov, 909/396-2171, Fax 909/396-2175) 21865 E. Copley Dr. Diamond Bar, CA 91765-4182.

(7.) Ventura County Air Pollution Control District (Doug Tubbs, doug@ vcmtss.mhs.compuserve.com, 805/662-6950, Fax 805/645-1444) .669 County Square Dr. 2nd floor Ventura, CA 93003-5417.

(8.) Bay Area Air Quality Management District (Rudy Zurrudo, rvz@ merkle.baqmd.gov, 415/749-4629, Fax 415/749-5101) 939 Ellis Street San Francisco, CA 94109.

(9.) ManTech Environmental Technology, Inc. (Dr. Hunter Daughtrey, Hunter@ epamail.epa.gov, 919/541-4540, Fax 919/541-3566) 2 Triangle Dr. Research Triangle Park, NC 27709. *Analyze canisters supplied by EPA.*

(10.) UCLA (Dr. Susanne Paulson, paulson@atmos.ucla.edu, 310/206-4442, Fax 310/206-5219) Department of Atmospheric Sciences, University of California, Los Angeles Los Angeles, CA 90095-1565. *Analyze canisters supplied by Desert Research Institute.*

(11.) Atmospheric Analytical Consultants (Dr. Sucha Parmar, sparmar@aol.com, 805/650-1642, Fax 805/650-1644) Ventura, CA

3.0 Specific Objectives and Approach

3.1 Review SOPs to identify differences in analytical methods and procedures that may cause differences in the data produced by participating laboratories. Aspects of SOPs to be reviewed by DRI will include cleaning and certifying canisters and samplers, calibration methods and reference materials, use and maintenance of dryers for water management, sample trapping and injection methods, choice of chromatographic column and operating conditions, peak integration procedure and selection of threshold, peak identification procedures, and data processing and management.

3.2 Assess stability of specific compounds in canisters over a time period comparable to the average holding time during the field study.

3.3 Determine significant systematic biases (greater than 30% for concentrations above 1.0 ppbC for individual compounds and greater than 20% for total nonmethane hydrocarbons) due to analytical methods and procedures. DRI will determine consistency in peak identification for individual species, total NMHC, and fraction of unidentified NMHC.

4.0 Management and Communication Protocol

4.1 Air Resources Board, Monitoring and Laboratory Division will arrange for collection of ambient samples.

4.2 Mike Miguel of the ARB will receive and forward data from participants to DRI for analysis.

4.2 Eric Fujita of DRI will prepare a summary report for review by participants.

5.0 Documentation

Each laboratory is to submit the following documentation to Eric Fujita: 1) description of collection and analysis methods and standard operating procedures for canister and sampler cleaning and certification, sample collection, sample analysis, data processing and management, quality control and assessment; 2) list of compounds in the retention time library; and 3) definition of minimum detection limits and measurement precision.

6.0 Performance Audit Samples

6.1 Each participating laboratory, except ManTech and UCLA, will supply cleaned, evacuated 6-liter canisters to ARB in El Monte, CA by May 30, 1997. Canisters are to be shipped to Pat Harrington at 9480 Telstar Avenue, Suite 4 El Monte, CA 91731. The following numbers of canisters are to be supplied by each laboratory.

2 canisters: AAC, BAAQMD, SCAQMD

3 canisters: BRC, SDAPCD, VCAPCD

4 canisters: ARB

5 canisters: DRI, EPA

Canisters should be labeled by each laboratory with an internal identification number. ARB will tag each canister with the following sampling information: laboratory, canister identification number, sampling site, date, start and end times, and sampling port number.

6.2 ARB will fill the canisters to 20-25 psi with ambient air from the Los Angeles area using the twelve-port manifold sampling system supplied by the Desert Research Institute. One set of canisters will be collected in the morning (after 6:00 a.m. and before 9:00 a.m., PDT) at the Los Angeles N. Main monitoring station to represent an area heavily influenced by mobile source emissions. The other set will be collected in the afternoon (after 1:00 p.m. and before 4:00 p.m., PDT) at the Azusa monitoring station to represent a downwind area with maximum ozone levels. In addition, a set of evening samples (after 6:00 p.m. and before 8:00 p.m.) will be collected at Santa Monica Beach to represent a background sample. The following sampling list indicates the relative positions of the samples to be collected by ARB.

LA, N. Main: AAC, ARB, BAAQMD, BRC, DRI, EPA, SCAQMD, SDAPCD, VCAPCD, ARB (duplicate), DRI (duplicate), EPA (duplicate)

Azusa: AAC, ARB, BAAQMD, BRC, DRI, EPA, SCAQMD, SDAPCD, VCAPCD, ARB (duplicate), DRI (duplicate), EPA (duplicate)

Santa Monica: BRC, DRI, EPA, SDAPCD, VCAPCD

6.3 Pat Harrington will send the tagged ambient audit samples to participating laboratory by June 4, 1997.

6.4 Each laboratory will analyze the audit samples within ten working days after receiving the audit canisters. EPA, ARB and DRI will reanalyze their primary samples after one and two months to monitor the stability of the audit samples. Upon completion of analysis, the two duplicate samples collected by DRI and EPA will be forwarded to UCLA and ManTech, respectively by June 20, 1997.

7.0 Data Submittal and Analysis

7.1 Each laboratory will send hardcopies of chromatograms and a data report (species identification, retention times, individual species concentrations in ppbC, and total nonmethane organic gases including unidentified hydrocarbons) to Mike Miguel by July 9, 1997 (by July 25 for UCLA and ManTech). The data should also be sent electronically in a spreadsheet or database format. To expedite and facilitate compilation and comparison of data, use the 6-character mnemonic shown in Table C-1 for species field names. The table of field names will be sent to each participating laboratory in both Excel and ASCII files for use in constructing the database/spreadsheet. The list of identified compounds should be those normally reported by each group (PAMS target list in most cases), or specified by contract. UCLA will report “total reactive carbon.” Mike Miguel will forward the data to DRI for analysis after receiving DRI’s analytical data.

7.2 Corrections to originally submitted data must be accompanied by sufficient documentation of the reasons.

7.3 Analysis of the data by DRI will include linear regression of data for each participating laboratory versus the average values (individual values exceeding two standard deviations of the mean of all values will be removed from the average). Differences in species concentrations of greater than 30% (for concentrations above 1 ppbC) between individual laboratories versus the adjusted mean values. Chromatograms will be examined to identify possible discrepancies in species identification.

7.4 Results will be sent to all participants for review and comments within three weeks after all data reports have been submitted. Each of the laboratories will be identified in the report by code only (letter code selected at random) in the draft report. The final report will contain the letter code key as an appendix.

Table 1
SCOS97 VOC Data Field Names (Mnemonics)

Sort No.	Compound Name [a]	Mnemonic	Flag	C_no	mw	convert to ug/m3
1	carbon monoxide (ppmv)	CO_PPM		1	28.01	1145.609
2	carbon dioxide (ppmv)	CO2PPM		1	44.01	1800.009
3	methane (ppmv)	METHAN		1	16.04	656.036
4	ethane	ETHANE	p	2	30.07	0.6149
5	ethene	ETHENE	p	2	28.05	0.5736
6	acetylene	ACETYL	p	2	26.04	0.5325
7	propene	PROPE	p	3	42.08	0.5737
8	propane	N_PROP	p	3	44.1	0.6012
9	Freon 12	FRE12	n	1	120.91	4.9452
10	isobutane	I_BUTA	p	4	58.12	0.5943
11	1-butene	LBUT1E	p	4	56.11	0.5737
12	iso-butene	LIBUTE	p	4	56.11	0.5737
13	1-butene&i-butene	BEABYL	p	4	56.11	0.5737
14	1,3-butadiene	BUDI13		4	54.09	0.5531
15	acetaldehyde	ACETAL	o	2	44.05	0.9008
16	n-butane	N_BUTA	p	4	58.12	0.5943
17	methanol (ppbv)	METOH	o	0.58	32.04	1.3104
18	t-2-butene	T2BUTE	p	4	56.11	0.5737
19	1&2-butyne	BUTYN		4	54.09	0.5531
20	c-2-butene	C2BUTE	p	4	56.11	0.5737
21	3-methyl-1-butene	B1E3ME		5	70.13	0.5737
22	ethanol (ppbv)	ETHOH	o	1.18	46.07	1.8843
23	acetonitrile	ACN	n	2	41.05	0.8395
24	isopentane	IPENTA	p	5	72.15	0.5902
25	acetone	ACETO	o	3	58.08	0.7918
26	1-pentene	PENTE1	p	5	70.13	0.5737
27	2-methyl-1-butene	B1E2M		5	70.13	0.5737
28	n-pentane	N_PENT	p	5	72.15	0.5902
29	isoprene	I_PREN	p	5	68.11	0.5571
30	t-2-pentene	T2PENE	p	5	70.13	0.5737
31	c-2-pentene	C2PENE	p	5	70.13	0.5737
32	2-methyl-2-butene	B2E2M		5	70.13	0.5737
33	F113	F113	n	2	187.38	3.8319
34	2,2-dimethylbutane	BU22DM	p	6	86.17	0.5874
35	2-methylpropanal	PRAL2M	o	4	72.07	0.7369
36	cyclopentene	CPENTE	p	5	68.11	0.5571
37	methacrolein	MEACRO	o	2	28.05	0.5736
38	4-methyl-1-pentene	P1E4ME		6	84.16	0.5737
39	3-methyl-1-pentene	P1E3ME		6	84.16	0.5737
40	cyclopentane	CPENTA	p	5	70.13	0.5737
41	2,3-dimethylbutane	BU23DM	p	6	86.17	0.5874
42	MTBE (ppbv)	MTBE	o	4.37	88.14	3.6049
43	2-methylpentane	PENA2M	p	6	86.17	0.5874
44	butanal	BUAL	o	4	72.12	0.7374
45	butanone	BUONE	o	4	72.12	0.7374
46	3-methylpentane	PENA3M	p	6	86.17	0.5874
47	2-methyl-1-pentene	P1E2ME	p	6	84.16	0.5737
48	1-hexene	HEX1E		6	84.16	0.5737
49	C6 olefin	C6OLE1		6	84.16	0.5737
50	n-hexane	N_HEX	p	6	86.17	0.5874
51	t-3-hexene + chloroform	T3HEXE		6	84.16	0.5737
52	c-3-hexene	C3HEXE		6	84.16	0.5737
53	t-2-hexene	T2HEXE		6	84.16	0.5737
54	2-methyl-2-pentene	P2E2ME		6	84.16	0.5737
55	c-2-hexene	C2HEXE		6	84.16	0.5737
56	cis-3-methyl-2-pentene	P2E3MC		6	84.16	0.5737
57	trans-3-methyl-2-pentene	P2E3MT		6	84.16	0.5737
58	3-methyl-2-pentene	P2E3ME		6	84.16	0.5737

59	2,2-dimethylpentane	PEN22M		7	100.2	0.5855
60	methylcyclopentane	MCYPNA	p	6	84.16	0.5737
61	2,4-dimethylpentane	PEN24M	p	7	100.2	0.5855
62	mechloroform	MECLOR	n	2	133.9	2.7383
63	2,2,3-trimethylbutane	BU223M		7	100.2	0.5855
64	1-methylcyclopentene	CPENE1		6	82.15	0.56
65	benzene	BENZE	p	6	78.11	0.5324
66	3,3-dimethylpentane	PEN33M		7	100.2	0.5855
67	cyclohexane	CYHEXA	p	6	84.16	0.5737
68	4-methylhexene	HEXE4M		7	98.19	0.5737
69	2-methylhexane	HEXA2M	p	7	98.19	0.5737
70	2,3-dimethylpentane	PEN23M	p	7	100.2	0.5855
71	cyclohexene	CYHEXE		6	82.15	0.56
72	3-methylhexane + pentanal	HEXA3M	p	7	100.2	0.5855
73	C7 olefin	C7OLE1		7	98.19	0.5737
74	1,3-dimethylcyclopentane	CPA13M		7	98.19	0.5737
75	3-ethylpentane	PA3ET		8	114.23	0.584
76	2,2,4-trimethylpentane	PA224M	p	8	114.23	0.584
77	C7 olefin	C7OLE2		7	98.19	0.5737
78	t-3-heptene	T3HEPE		7	98.19	0.5737
79	n-heptane	N_HEPT	p	7	100.2	0.5855
80	C8 olefin	C8OLE1		8	112.21	0.5737
81	C8 olefin	C8OLE2		8	112.21	0.5737
82	C8 olefin	C8OLE3		8	112.21	0.5737
83	2,4,4-trimethyl-1-pentene	P1E244		8	112.21	0.5737
84	methylcyclohexane	MECYHX	p	7	98.19	0.5737
85	C8 paraffin	C8PA1		8	114.23	0.584
86	2,5-diemthylhexane	HEX25M		8	114.23	0.584
87	2,4-diemthylhexane	HEX24M		8	114.23	0.584
88	C8 paraffin	C8PA2		8	114.23	0.584
89	2,3,4-trimethylpentane	PA234M	p	8	114.23	0.584
90	toluene	TOLUE	p	7	92.14	0.5384
91	2,3-dimethylhexane	HX23DM		8	114.23	0.584
92	2-methylheptane	HEP2ME	p	9	128.26	0.5829
93	4-methylheptane	HEP4ME		9	128.26	0.5829
94	C8 paraffin	C8PA3		8	114.23	0.584
95	3-methylheptane	HEP3ME	p	8	114.23	0.584
96	hexanal	HEXAL	o	6	100.16	0.6828
97	2,2,5-trimethylhexane	HEX225		9	128.26	0.5829
98	octene-1	OCT1E		8	112.21	0.5737
99	1,1-dimethylcyclohexane	CHX11M		8	112.21	0.5737
100	n-octane	N_OCT	p	8	114.23	0.584
101	2,3,5-trimethylhexane	HEX235		9	128.26	0.5829
102	2,4-dimethylheptane	HEP24D		9	128.26	0.5829
103	4,4-dimethylheptane	HEP44D		9	128.26	0.5829
104	2,6-dimethylheptane	HEP26D		9	128.26	0.5829
105	2,5-dimethylheptane	HEP25D		9	128.26	0.5829
106	3,3-dimethylheptane	HEP33D		9	128.26	0.5829
107	C9 olefin	C9OLE1		9	126.24	0.5737
108	C9 olefin	C9OLE2		9	126.24	0.5737
109	ethylbenzene	ETBZ	p	8	106.16	0.5427
110	C9 olefin	C9OLE3		9	126.24	0.5737
111	m- & p-xylene	MP_XYL	p	8	106.16	0.5427
112	2-methyloctane	OCT2ME		9	128.26	0.5829
113	3-methyloctane	OCT3ME		9	128.26	0.5829
114	C9 paraffin	C9PAR1		9	128.26	0.5829
115	styrene + heptanal	STYR	p	8	104.14	0.5324
116	o-xylene	O_XYL	p	8	106.17	0.5428
117	nonene-1	NONE1		9	126.24	0.5737
118	C9 paraffin	C9PAR2		9	128.26	0.5829
119	n-nonane	N_NON	p	9	128.26	0.5829
120	C9 paraffin	C9PAR3		9	128.26	0.5829

121	C9 olefin	C9OLE4		9	126.24	0.5737
122	C9 paraffin	C9PAR4		9	128.26	0.5829
123	isopropylbenzene	IPRBZ	p	9	120.2	0.5462
124	isopropylcyclohexane	IPCYHX		9	126.24	0.5737
125	alpha-pinene	A_PINE		10	136.23	0.5572
126	benzaldehyde	BZALDE	o	7	106.1	0.6199
127	2,6-dimethyloctane	OCT26D		10	142.29	0.582
128	C10 olefin	C10OL1		10	140.27	0.5737
129	3,6-dimethyloctane	OCT36M		10	142.29	0.582
130	n-propylbenzene	N_PRBZ	p	9	120.2	0.5462
131	m-ethyltoluene	M_ETOL	p	9	120.2	0.5462
132	p-ethyltoluene	P_ETOL	p	9	120.2	0.5462
133	1,3,5-trimethylbenzene	BZ135M	p	9	120.2	0.5462
134	C10 paraffin	C10P_A		10	142.29	0.582
135	o-ethyltoluene	O_ETOL	p	9	120.2	0.5462
136	octanal	OCTAL	o	8	128	0.6544
137	beta-pinene	B_PINE		10	136.23	0.5572
138	1,2,4-trimethylbenzene	BZ124M	p	9	120.2	0.5462
139	n-decane	N_DEC	p	10	142.29	0.582
140	C10 aromatic	C10AR1		10	134.22	0.549
141	isobutylbenzene	I_BUBZ		10	134.22	0.549
142	sec-butylbenzene	S_BUBZ		10	134.22	0.549
143	C10 olefin	C10OL2		10	140.27	0.5737
144	1,2,3-trimethylbenzene	BZ123M	p	9	120.2	0.5462
145	C10 paraffin	C10P_C		10	142.29	0.582
146	limonene	LIMON		10	136.24	0.5572
147	indan	INDAN		9	118.17	0.537
148	indene	INDENE		9	116.15	0.5278
149	m-diethylbenzene	DETBZ1	p	10	134.22	0.549
150	C10 aromatic	C10AR2		10	134.22	0.549
151	p-diethylbenzene	DETBZ2	p	10	134.22	0.549
152	n-butylbenzene	N_BUBZ		10	134.22	0.549
153	o-diethylbenzene	DETBZ3	p	10	134.22	0.549
154	C10 aromatic	C10AR3		10	134.22	0.549
155	1,3-dimethyl-4-ethylbenzene	BZDME		10	134.22	0.549
156	C10 aromatic	C10AR4		10	134.22	0.549
157	isopropyltoluene	IPRTOL		10	134.22	0.549
158	nonanal	NONAL	o	9	142	0.6453
159	n-undecane	N_UNDE	p	11	156.3	0.5812
160	C10 aromatic	C10AR5		10	134.22	0.549
161	C10 aromatic	C10AR6		10	134.22	0.549
162	C11 paraffin	C11P_A		11	156.32	0.5812
163	1,2,4,5-tetramethylbenzene	BZ1245		10	134.22	0.549
164	1,2,3,5-tetramethylbenzene	BZ1235		10	134.22	0.549
165	C11 paraffin	C11P_B		11	156.32	0.5812
166	2-methylindan	IND_2M		10	132.21	0.5407
167	1-methylindan	IND_1M		10	132.21	0.5407
168	C11 aromatic	C11AR1		11	148.22	0.5511
169	C11 aromatic	C11AR3		11	148.22	0.5511
170	naphthalene	NAPHTH		10	128.16	0.5242
171	n-dodecane	N_DODE		12	170.34	0.5806
	Total Identified NMHC	IDNMHC		1		
	Unidentified [b]	UNID		1	13.85	0.5665
	Total NMHC	TNMHC				
	Identified oxygenated (ppbv) [c]	IDOXY		1		

a. Unless otherwise indicated, conversions to ug/m3 assume data are in ppbC.

b. Sum of unidentified hydrocarbons. Excludes halogenated and oxygenated compounds.

c. Sum of MTBE, methanol, and ethanol.

Flags: p - PAMS target list; o - oxygenated compounds; n - non-hydrocarbon compounds.